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FT-Raman and FT-IR vibrational spectroscopic studies of nanocrystalline Ba_2RESbO_6 (RE = Sm, Gd, Dy and Y) perovskites

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ABSTRACT

The nanoparticles of Ba_2RESbO_6 (RE = Sm, Gd, Dy and Y) were synthesized using auto ignition combustion process. The structure and phase purity of the as-prepared nanopowders were examined by X-ray diffraction pattern. A systematic analysis of the structure of the four compounds was carried out for the first time by recording Raman and IR spectra. The four Raman active modes A_{1g}, E_g and $2F_{2g}$ were observed as strong or medium intense bands in the Raman spectra and the IR active $F_{1u}(1)$ mode is obtained as a strong absorption band around 630 cm^{-1} in all the four compounds. Hence it is confirmed that the above compounds were crystallized in the cubic symmetry with $Fm\bar{3}m$ space group.

1. Introduction

Perovskite oxide type materials are found to have considerable importance in condensed matter science, due to the diversity in their crystal structures. Among these materials, a series of Ba_2LnSbO_6 (Ln = Lanthanides) compounds were studied by different research groups [1,2]. Paulose et al. [3] and Kurian et al. [4] reported that some of these compounds are suitable substrate materials for $YBa_2Cu_3O_{7-\delta}$ films by developing high quality superconducting thick films on these substrates. In order to fully realize the potential applications of Ba_2RESbO_6 compounds, it is essential to establish their precise structures. Alonso et al. [5], Fu and IJdo [6] and Karunadasa et al. [7] studied the crystal structure of Ba_2RESbO_6 (RE = Sm, Gd, Dy and Y) materials using X-ray and neutron diffraction patterns by Rietveld analysis and reported that they have double cubic perovskite structure. Jose et al. have reported that Ba_2LaSbO_6 has monoclinic structure [8]. Recently, Saines et al. [9] examined the entire series of the compounds using Synchrotron X-ray diffraction and reported that Ba_2RESbO_6 with the largest lanthanides, La–Nd, showed rhombohedral symmetry with space group $R\bar{3}$ and smaller lanthanides Sm–Lu and Y showed cubic symmetry with space group $Fm\bar{3}m$. In all the above studies on these antimonate systems, conventional solid state synthesis route were used for the preparation of their single phase compounds which involves prolonged calcination at high temperatures (>1200 °C) with intermediate grindings, yielding large coarse grained micron sized powders. In this paper, we report the structural analysis of nanocrystalline Ba_2RESbO_6 (RE = Sm, Gd, Dy and Y) compounds synthesized by a modified combustion method using X-ray diffraction, FT-Raman and FT-IR vibrational spectroscopy.

2. Experimental

To prepare Ba_2RESbO_6 by the combustion method [10], an aqueous solution containing ions of RE, Ba and Sb was prepared by dissolving stoichiometric amounts of RE_2O_3 in dilute nitric acid, $Ba(NO_3)_2$ in water and Sb_2O_3 in boiling tartaric acid. To get the precursor complex, citric acid was added to the solution containing the metal ions, maintaining the citric acid to the cation ratio at unity. The oxidant/fuel ratio of the system was adjusted by using nitric acid and ammonium hydroxide, and the ratio was kept at unity. The solution containing the complex precursor mixture at a pH of ~7.0 was heated using a hot plate at ~250 °C in a ventilated fume hood. The solution boils on heating and undergoes dehydration and decomposition leading to a smooth deflation and producing foam. The foam then ignites by itself on persistent heating giving voluminous and fluffy product of combustion. The combustion product was subsequently characterized as single-phase nanocrystals of Ba_2RESbO_6. Structure of the as-prepared powder and the sintered product was examined by powder X-ray diffraction (XRD) technique using a X-ray Diffractometer (Model Bruker D-8) with Nickel filtered CuK_α radiation. The FT-Raman measurements of the nanocrystalline Ba_2RESbO_6 (RE = Sm, Gd, Dy and Y) were carried out at room temperature over the wavenumber range 50–900 cm^{-1} using Bruker RFS/100S Spectrometer at a power level of 150 mW and at a resolution of 4 cm^{-1}. The samples were excited with an Nd:YAG laser lasing at 1.064 nm and the scattered radiations were detected using a Ge detector. The infrared (IR) spectra of the samples were recorded over the range 400–4000 cm^{-1} on a Thermo-Nicolet Avatar 370 Fourier Transform Infrared (FT-IR) Spectrometer using KBr pellet method.

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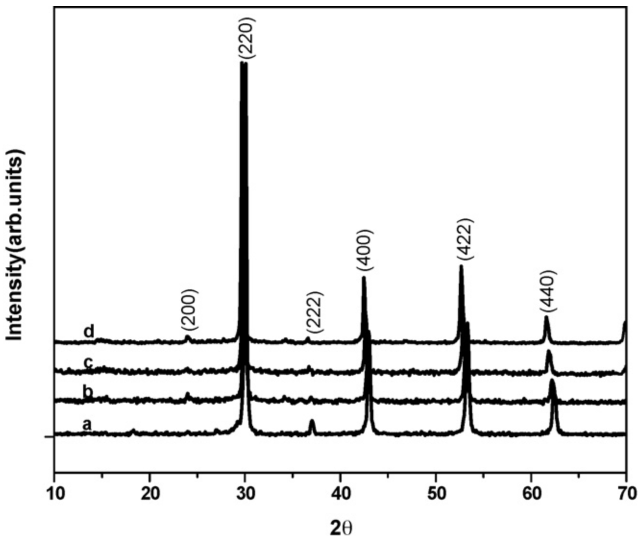

Fig. 1. X-ray diffraction patterns of powders of (a) Ba$_2$YSbO$_6$, (b) Ba$_2$DySbO$_6$, (c) Ba$_2$GdSbO6 and (d) Ba$_2$SmSbO$_6$.

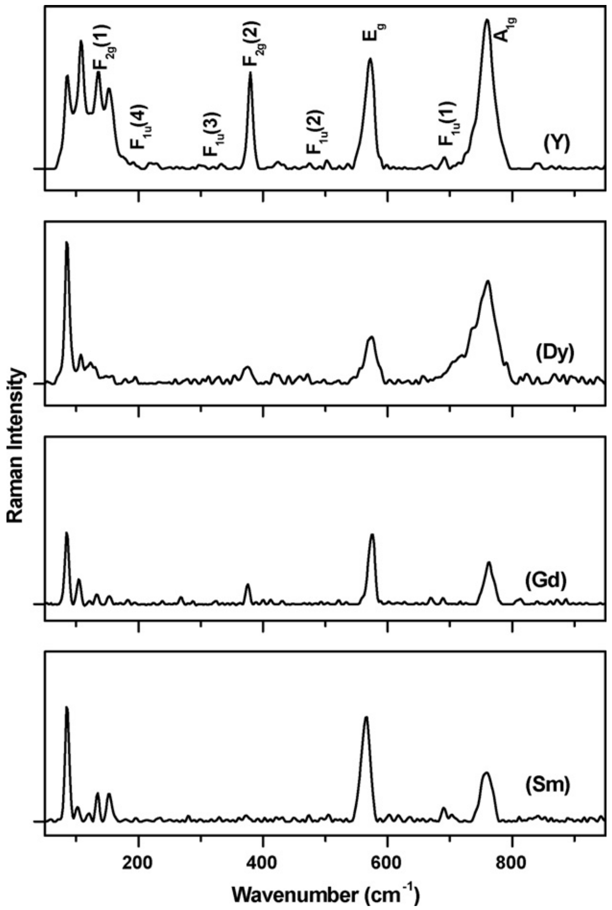

Fig. 2. Raman spectra of nanocrystalline Ba$_2$RESbO$_6$ (RE = Sm, Gd, Dy and Y).

3. Factor group analysis

The X-ray diffraction patterns of the four nanocrystalline compounds are shown in Fig. 1. The X-ray diffraction study reveals that all the four compounds have cubic symmetry and belongs to the space group $Fm\bar{3}m$ with $Z = 4$ and $Z^B = 1$. Saines et al. [8] has also reported that these compounds have $Fm\bar{3}m$ cubic symmetry through neutron and synchrotron X-ray diffraction studies. The group theoretical analysis using the standard correlation method gives 27 normal modes of vibration, exclusive of the 3 acoustical modes [11–13]. They are distributed as

$$\Gamma = \mathrm{A_{1g}(R) + E_g(R) + F_{1g}(silent) + 2F_{2g}(R) + 4F_{1u}(IR)} + F_{2u}\mathrm{(silent)}$$

4. Results and discussion

The FT-Raman and FT-IR spectra of the nanocrystalline Ba$_2$RESbO$_6$ (RE = Sm, Gd, Dy and Y) samples are shown in Figs. 2 and 3. The observed bands (cm^{-1}) in the Raman spectra, their relative intensities and the band assignments are given in Table 1. The IR bands characteristic of the samples is tabulated in Table 2.

For comparison, the FT-IR spectra of the coarse grained powders of Ba$_2$YSbO$_6$ and Ba$_2$SmSbO$_6$ prepared by conventional solid state route [3,4] were also recorded and are given in Figs. 4 and 5. In both the compounds, the IR spectra of nanocrystalline powders and coarse grained powders are found to be identical. This confirms that phase pure materials are formed in the combustion method.

According to the group theoretical analysis, the complex perovskite A$_2$BB′O$_6$ with a cubic space group $Fm\bar{3}m$ has only four Raman active modes A$_{1g}$, E$_g$ and 2F$_{2g}$. The Raman spectra of all the four samples show strong or medium intense bands at about 760, 572, 375 and 108 cm^{-1} and several weak bands at different wavenumbers. The four strong bands in the Raman spectra are assigned to the four Raman active modes [12] and the weak bands may be due to the IR active F$_{1u}$ modes that have become active due to the lowering of the site symmetry.

The symmetric and asymmetric stretching vibrations of BO$_6$ or B′O$_6$ octahedron give the A$_{1g}$ and E$_g$ modes, respectively. During these modes of vibration, all the cations remains at rest and the oxygen atoms move along the B–O–B′ axis thereby generating strong peaks at relatively high frequencies. In all the four compounds, the symmetric stretching A$_{1g}$ mode is observed as sharp intense band at 759, 763, 761 and 760 cm^{-1}, respectively. The sharp and strong A$_{1g}$ mode indicates high degree of long range ordering [13]. In the IR spectra, this IR inactive mode appears as a very weak band at 858 cm^{-1} in the compounds Ba$_2$SmSbO$_6$, Ba$_2$GdSbO$_6$ and Ba$_2$YSbO$_6$ and at 856 cm^{-1} in the compound Ba$_2$DySbO$_6$ [14]. Very weak counterparts are also found in the Raman spectra around 820 cm^{-1}. The

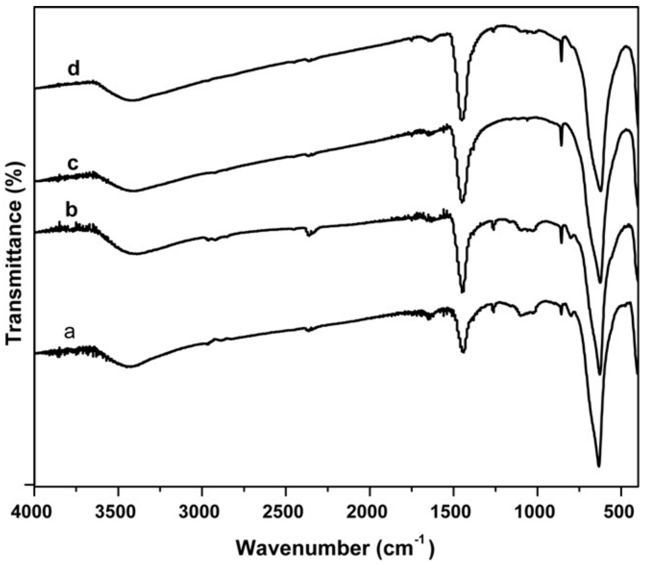

Fig. 3. FT-IR spectra of nanopowders of (a) Ba$_2$YSbO$_6$, (b) Ba$_2$DySbO$_6$, (c) Ba$_2$GdSbO$_6$ and (d) Ba$_2$SmSbO$_6$.

Table 1
The observed bands (cm^{-1}), their relative intensities and the band assignments of the Raman spectra.

Relative intensities and wavenumbers of compounds				Band assignments
Ba_2SmSbO_6	Ba_2GdSbO_6	Ba_2DySbO_6	Ba_2YSbO_6	
812 vw	812 vw	826 vw		
		789 w		
759 s	762 s	761 vs	760 vvs	
		738 sh		A_{1g}
		721 sh		
690 w	688 vw			
	671 w		691 w	$F_{1u}(1)$
566 vs	575 vs	574 s	572 vs	E_g
		554 sh		
473 vw	432 vw	471 w	476 vw	
	413 vw	457 vw	423 w	$F_{1u}(2)$
	400 vw	441 vw		
		417 w		
372 vw	375 m	375 m	380 vs	$F_{2g}(2)$
329 vw		329 vw	332 vw	
		312 vw	307 vw	$F_{1u}(3)$
280 vw		281 vw		
	268 vw			
			219 w	
	182 vw	195 vw	190 vw	$F_{1u}(4)$
		179 vw	171 vw	
153 m	153 w	157 vw	153 m	
134 m	133 w	133 sh	136 s	
120 w		123 m		
102 w	105 m	108 m	108 vs	$F_{2g}(1)$
85 vs	85 vs	85 vvs	86 s	

Relative intensity: vs, very strong; s, strong; m, medium; vw, very weak; w, weak and sh, shoulder.

Table 2
The observed bands (cm^{-1}) in the range 860–620 cm^{-1}, their relative intensities and the band assignments of the IR spectra.

Compound	A_{1g} mode (cm^{-1})	F_{1u} mode (cm^{-1})
Ba_2SmSbO_6	858 w	623 s
Ba_2GdSbO_6	858 w	627 s
Ba_2DySbO_6	856 w	629 s
Ba_2YSbO_6	858 w	634 s

Relative intensity: w, weak; s, strong.

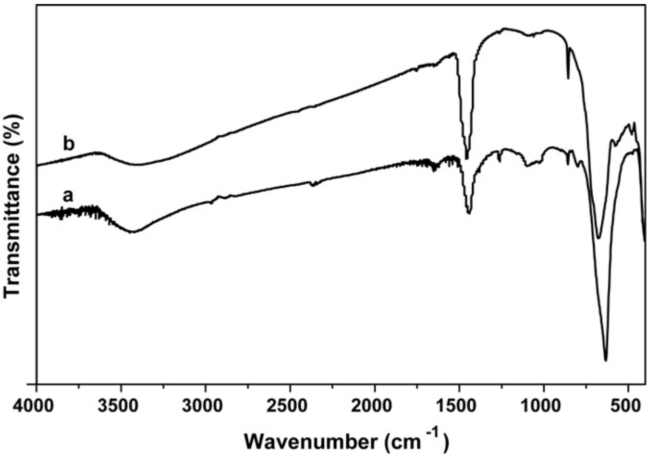

Fig. 4. FT-IR spectrum of (a) nanopowder of Ba_2YSbO_6 and (b) coarse-grained powder of Ba_2YSbO_6 prepared by solid-state route.

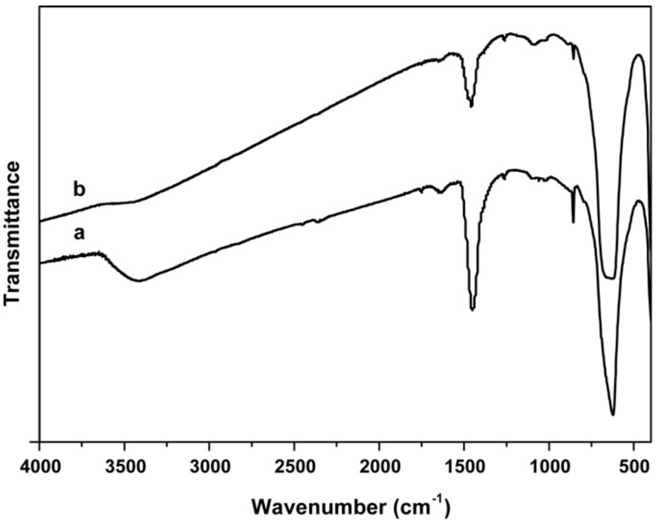

Fig. 5. FT-IR spectrum of (a) as-prepared Ba_2SmSbO_6 powder obtained through combustion synthesis (b) Ba_2SmSbO_6 powder.

highly intense band around 572 cm^{-1} in all the four spectra are assigned to the doubly degenerate E_g mode of vibration. The E_g mode is also observed as strong intense band.

It is interesting to note that the A_{1g} mode and E_g mode show similar variation in wavenumbers as the B cation changes from Y to Sm as shown in Fig. 6. The ionic radii of the rare earth elements, the tolerance factor, the wavenumbers of A_{1g} and E_g modes are tabulated in Table 3.

As the tolerance factor decreases, the wavenumbers of A_{1g} and E_g mode increases, when the rare earth changes from Y to Gd. However, in Ba_2SmSbO_6 the corresponding bands are shifted to lower wavenumbers. The structural study [9] shows that Ba_2RESbO_6 compounds with RE = La–Nd has rhombohedral symmetry with space group $R\bar{3}$ and that with RE = Sm–La and Y has cubic symmetry with space group $Fm\bar{3}m$. The transition from rhombohedral to cubic symmetry occurs between Nd and Sm compounds. The shift of the A_{1g} and E_g modes of Ba_2SmSbO_6, to lower wavenumbers, when compared to the other three compounds may be due to its existence at the boarder of symmetry transition.

The F_{2g} modes are also sensitive to long range ordering and are contributed by the allowed transition of the A cation. The $F_{2g}(1)$ mode is expected in the low frequency range 50–150 cm^{-1} [13].

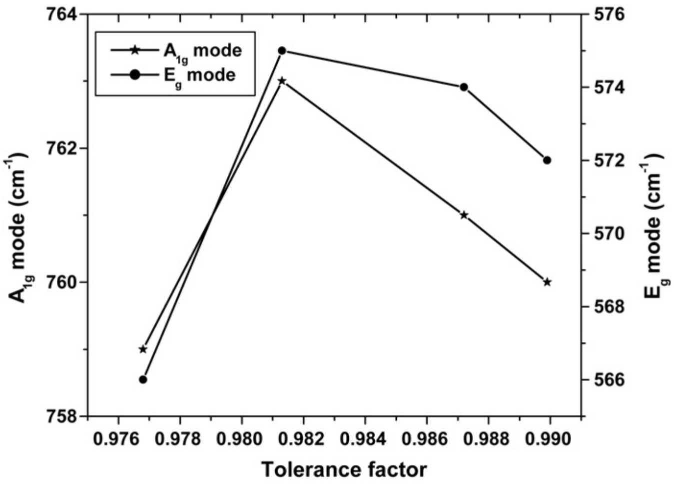

Fig. 6. Variation of A_{1g} and E_g mode wavenumbers of the four compounds with the tolerance factors.

Table 3
The ionic radii of the rare earth elements, the tolerance factor, the wavenumbers of A_{1g}, E_g and $F_{1u}(1)$ modes.

Compound	Ionic radii of the rare earths (Å)	Tolerance Factor (t)	A_{1g} (cm^{-1}) (Raman)	E_g (cm^{-1}) (Raman)	$F_{1u}(1)$ (cm^{-1}) (IR)
Ba_2SmSbO_6	0.958	0.9768	759	566	623
Ba_2GdSbO_6	0.938	0.9813	763	575	627
Ba_2DySbO_6	0.912	0.9872	761	574	629
Ba_2YSbO_6	0.900	0.9899	760	572	634

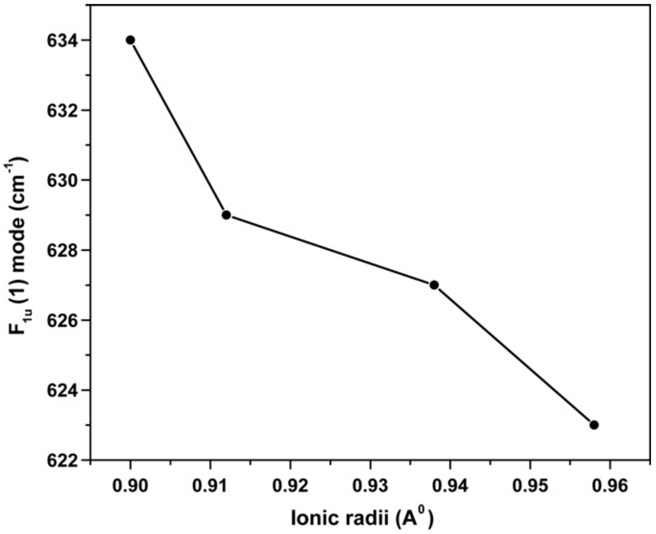

Fig. 7. Variation of $F_{1u}(1)$ mode wavenumbers with the B cation ionic radii of the Ba_2RESbO_6.

The spectra of all the four compounds show three to four medium intense bands in this region. For a given cation, the frequency of this mode is essentially related to the cell parameters irrespective of the chemical nature of the B cations [15,16]. Taking into consideration the intensity and the wavenumbers, the bands in the range 157–85 are assigned to the $F_{2g}(1)$ mode. Thus triply degenerate $F_{2g}(1)$ Raman active mode shows three or four intense to medium intense bands, all almost of the same wavenumbers [11]. The strong band in the region 375 cm^{-1} in all the four compounds is due to the $F_{2g}(2)$ mode of vibration.

The Raman spectrum of Ba_2DySbO_6 shows slight difference when compared to the spectra of the other three compounds. In Ba_2DySbO_6, the A_{1g} mode develops an asymmetry in the shape of the band. The band is broadened and shows incomplete splitting with redshifted shoulders at 738 and 721 cm^{-1}. The splitting of the $F_{2g}(1)$ mode has almost disappeared and the band attains a diffused character. The E_g mode of vibration also appears to be slightly broadened. These changes in the spectrum may be due to the tilting or distortion of the $B/B'O_6$ octahedron [12].

The IR active F_{1u} mode is observed as very strong absorption band around 630 cm^{-1} in the IR spectrum of all the four samples [17]. In Ba_2SmSbO_6, Ba_2GdSbO_6, Ba_2DySbO_6 and Ba_2YSbO_6, this mode is observed at 623, 627, 629 and 634 cm^{-1}, respectively. This shift can be correlated to the ionic radii of the B cations. The B—O bond length and hence the volume of the BO_6 cation increases as the ionic radii increases from Y to Sm. This accounts for the gradual shift of the $F_{1u}(1)$ mode to the lower wavenumber side as we go from Ba_2YSbO_6 to Ba_2SmSbO_6. This is shown in Fig. 7. In the Raman spectra, this mode appears as very weak bands around 690 cm^{-1}. The triply degenerate $F_{1u}(2)$, $F_{1u}(3)$ and $F_{1u}(4)$ modes also appear as very weak bands in the Raman spectra.

5. Conclusion

The FT-Raman and FT-IR spectra of Ba_2RESbO_6 (RE = Sm, Gd, Dy and Y) compounds are recorded and analysed. The four Raman active modes A_{1g}, E_g and $2F_{2g}$ are observed as strong and medium intense bands in the Raman spectra of all the four compounds. The IR active $F_{1u}(1)$ mode is obtained as a strong absorption band around 630 cm^{-1}. Hence we can definitely conclude that all the four nanocrystalline Ba_2SmSbO_6, Ba_2GdSbO_6, Ba_2DySbO_6 and Ba_2YSbO_6 compounds have cubic symmetry with $Fm\bar{3}m$ space group.

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